MICRO-ANALYSIS TECHNIQUES FOR THE CHARACTERIZATION OF INDIVIDUAL ENVIRONMENTAL PARTICLES

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Abstract

Although micro- and surface analysis techniques are nowadays routinely applied in various fields, they are seldom invoked in environmental research in spite of the importance of particles in the environment. An outline is given of the potential and relevant methodology of electron microprobe analysis, scanning proton microprobe analysis, secondary ion mass spectrometry and laser microprobe mass spectrometry. The use of these techniques for atmospheric and aqueous particles is illustrated with literature examples.

Keywords

Micro-analysis, environment, aerosols, EPXMA, SPM, LAMMS, SIMS

Nowadays, micro-analytical techniques are very important in material science, corrosion studies, micro-electronics and other advanced fields of research. In studies on environmental particles, however, microbeam analysis techniques are still invoked very seldom. This is rather surprising in view of the importance that particles have in the environment. Indeed, individual particle characterization can reveal whether a specific element or compound is uniformly distributed over all the particles of a population or whether it is a component of only a specific group of particles. Sometimes even the element-distribution within a particle can be inferred. In this way it becomes more straightforward to assign particles to specific sources, while more refined information about source mechanisms and heterogeneous surface reactions can often be derived.

Below we will give a brief overview of some techniques for individual environmental particle analysis based on the characteristic physical interactions between electrons, ions or photons and the specimen.

AUTOMATED ELECTRON MICROPROBE ANALYSIS

Instruments for electron probe X-ray micro-analysis (EPXMA) or electron microscopy with energy-dispersive X-ray analysis attachments (SEM/EDX) can measure the X-ray photons generated in a μm -size sample to derive information on the sample area composition, in addition to its morphology. The theory for EPXMA and SEM/EDX analysis is described in several textbooks.

To study particulate samples by individual particle analysis requires the measurements of a large population set in order to obtain statistically meaningful data. At the Micro- and Trace Analysis Centre of the University of Antwerp, a JEOL Superprobe JXA - 733 is automated with a system for the automated particle recognition and characterization (PRC). An electron beam is raster-scanned over a preset sample area by means of a digital beam control. A particle is detected when the electron backscattered signal of the closed particle contour points exceeds a preset threshold value. An X-ray spectrum can be accumulated while performing cross scans over the particle. Thus the PRC program is set up in three sequential steps: localizing, sizing and chemical characterization, after which the beam scans for the next particle. In automated EPXMA, 500 particles can be multi-element analyzed in less than 2.5 hours, while the relative detection limit is about 0.1 %.

SCANNING PROTON MICROPROBE ANALYSIS

In the Scanning Proton Microprobe (SPM), a proton beam with an energy of 1 to 3 MeV is finely focused in the sample by means of magnetic quadrupoles and/or electrostatic lenses. The high energy proton beam is obtained with cyclotrons or Van de Graaff accelerators. Most SPM instruments provide routinely a spatial resolution of 0.5 to 10 μm . There are several processes occurring during the interaction of the proton beam with the sample.

In Particle Induced X-Ray Emission (PIXE) analysis, a Si(Li) detector collects X-rays for each beam position while the beam scans over the sample, and an on-line sorting process makes it possible to obtain real time X-ray intensity imaging. These elemental maps of the sample

being analyzed are similar to these obtained with EPXMA instruments. Accuracy of 10 to 20 percent is obtained for absolute analysis at detection limits down to 10 ppm.

In Rutherford Backscattering (RBS) analysis, the elastic back scattering of protons is used to obtain quantitative analysis of light elements like carbon, nitrogen and oxygen. A semiconductor surface barrier detector is often used. It is also possible to make elemental maps of C, N and O in real time, simultaneously with the trace element elemental maps. This has shown to be very useful to measure the stoichiometry of compounds in atmospheric aerosol particles [1].

The SPM is a recent technique, and most of the applications are in biology, archaeology, geology and material sciences. Artaxo et al. [1] showed the feasibility of a combined approach of EPXMA, LAMMS and SPM analysis of individual aerosol particles.

LASER MICROPROBE MASS SPECTROMETRY

Laser microprobe mass spectrometry (LAMMS) is based on the mass spectrometric analysis of ions, formed by the interaction of the sample with a high power density pulsed laser beam. In the LAMMA-500 instrument of Leybold-Heraeus, Cologne, Germany, a Nd-YAG laser generates very short and intense light pulses for vaporization and ionization of a microvolume of the sample. The power density is 10^7 – 10^{11} W/cm² for a 1 μ m laser focus and can be reduced to 2 % of its initial value by a 25 step attenuating filter system. This is especially interesting for particle surface analysis. Either positive or negative ions which are formed by laser irradiation of the selected sample area can be accelerated by a potential of 3000 V into a field-free drift region of the time-of-flight (TOF) mass spectrometer, and detected. The signal is fed into a 32 kbyte memory transient recorder and digitized. Spectra are stored in a personal computer for off-line data handling. Generally the LAMMS technique has various interesting features: it can detect all elements, and, compared to other microchemical techniques, detection limits are low. It can give indications concerning stoichiometry or inorganic speciation, and information about several organic compounds of environmental importance. Disadvantages are the facts that the technique is destructive and rather irreproducible and that the theoretical aspects of ion formation and behaviour in the system are not yet elucidated, which hampers quantitative analysis significantly.

SECONDARY ION MASS SPECTROMETRY

Secondary ion mass spectrometry (SIMS) is based on the bombardment of a sample surface by primary ions (Ar⁺, O⁺, etc.) or molecules generated in a duoplasmatron (energies in the keV range). Only a small fraction (typically 0.01–1%) of the sputtered atoms are charged. These secondary ions are attracted to a mass spectrometer. The separated positive or negative secondary ions are collected as mass spectra, as in-depth profiles or line-scans, or as distribution images of the sputtered surface. A mass spectrum can range from hydrogen to an m/z ratio of several hundreds.

SIMS offers special capabilities for particle analysis. The capabilities of SIMS include: detection of all elements, compound detection, isotope ratio measurements, depth profiling and ion imaging of specific constituents. The absolute detection limit for SIMS analysis is about 10^{-15} g for most elements and chemical compounds, and for anions down to 10^{-18} g. When molecular information of particles is needed, both LAMMS and SIMS can be used since they exhibit qualitatively the same positive ions.

APPLICATIONS

Although the number of relevant publications is not very high, it is not possible to give a complete and thorough literature review within the space allotted for this paper. For this, we refer to a recent publication of ours [2]. Rather we will review below only the work on single environmental particle analysis that has been published over the last ten years by the Micro- and Trace Analysis Centre of the University of Antwerp.

Remote aerosols

The aerosol composition of extremely remote locations is a subject of interest. Indeed, due to the growing industrialization and the long-range transport of pollutants, it has become increasingly difficult to define the composition of baseline natural aerosols in the absence of any pollution.

The Antarctic continent is probably the most convenient place on earth to study the composition of background aerosols because it is the most distant area from the world's predominant pollution sources and local anthropogenic contributions are negligible. Hierarchical and non-hierarchical cluster analyses were performed on individual coastal Antarctic aerosols using EPXMA [3]. The results show a domination of marine components in both the fine and the coarse mode fractions. Only a minor crustal component was found and thus crustal weathering processes must be far less important than the strength of the marine source. LAMMS of similar aerosol particles [4] revealed the presence of salts derived from methane sulphonic acid, a reaction product of the photo-oxidation of dimethylsulphide, which originates from the metabolism of certain marine algae and contributes significantly to the

global sulphur cycle.

Surkyn et al. [5] performed LAMMS on aerosol particles from the uplands of central Bolivia. The sampling station was located at 5230 m above sea level. In the immediate surroundings, the ground over a wide area is stony, partly snow-covered year-round and without vegetation. Particles from this site were soil derived aluminosilicates and/or Ca-rich particles and, in the smallest size fraction, ammonium sulphates. Occasionally, K- and C-rich particles were detected; most probably they resulted from forest burning.

Biogenic aerosols

It has already been hypothesized that the forest is a major source of aerosols in both the fine and coarse fractions. As part of the Global Tropospheric Experiment of NASA, individual aerosol particles sampled over the Amazon Basin were analyzed by automated EPXMA in order to study the processes of aerosol and gas emissions by the forest and to assess the chemical mechanisms occurring in the Amazon Basin atmosphere [3]. According to the methodology of Bernard et al. [6], hierarchical and non-hierarchical cluster techniques were applied to the whole data set for the classification of all particles. Most of the particle types could be related to two prevalent local sources, namely soil dust and biologically derived material. The former type is typically composed of Al, Si and Ti. The latter type is identified by the high Bremsstrahlung background (low-Z elements) and the presence of elements as Na, S, K, Cl, P, Ca and Zn or a combination of them. Particle types containing mainly S, K and P can be related to aerosol emissions by vegetation. LAMMS spectra of Amazon Basin aerosols are very complex due to the presence of different organic compounds, fragmented to various extents: sulphate salts of amines, methane sulphonate and fragmentation patterns of hydrocarbons, terpenes and phospholipids have been identified up to now [7][8]. Part of this organic material was found to be associated with inorganic salt mixtures consisting of plant nutrients, which points to a plant-transpiration origin. Another interesting result is the association of some trace elements (e.g. Pb and Zn) with the organics. Micro-PIXE and RBS were used simultaneously on Amazon Basin aerosol particles. It was easy to measure elements like Rb, Zn and Mn with concentrations below 10 ppm in individual particles.

Marine aerosols

In a first approach, LAMMS and EPXMA have been used to characterize individual North Sea aerosols [9]. With the aid of EPXMA, about 2,500 particles, sampled from a research vessel, were sized, chemically analyzed and classified. Sea salt appeared to be the most abundant particle type when the collected air masses originated from over the Atlantic Ocean and travelled toward the continent. Contrarily, in air masses that spent longer residence times over the continent, high concentrations of aluminosilicate particles (mostly spherical flyash particles), carbonaceous particles, CaSO_4 and spherical iron oxides were observed. LAMMS was applied to a number of representative particles in order to elaborate trace element contents and surface layer composition. Applying low energy laser shots to the spherical flyash particles revealed typical mass spectra that were interpreted as fingerprints for the desorption of polynuclear aromatic hydrocarbons (PAH). The most typical marine aerosol particles were of course seasalt particles, formed by the bubble bursting mechanism. Spectra of "pure" seasalt were dominated by Na, K, and typical Na/K/Cl cluster ions. Often, seasalt particles were found to have been transformed to some extent; in this case, nitrate and sulphate coatings were readily detectable [10]. Using LAMMS, Otten et al. [11][12] found the relative abundances of nitrate- and ammonium-rich particles in the North Sea aerosol to increase dramatically under the influence of polluted air masses. Recently, EPXMA characterizations were performed on a data set of more than 25,000 individual aerosols collected over the North Sea and the English Channel [13]. Differences between samples were studied on the basis of abundance variations using Principal Component Analysis. Nine different particle types were classified and they all were source apportioned unambiguously. The release of seasalt into the atmosphere is dominated by the process of breaking waves and this is more effective as the relative wind speed increases. Transformed seasalt particles rich in S are formed by the conversion reaction of NaCl into Na_2SO_4 implying the release of HCl into the atmosphere. S-rich particles of various composition, namely H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, were assigned to originate from anthropogenic sources and they are probably formed by gas-to-particle conversion. Also the CaSO_4 particles above the North Sea are predominantly emitted by anthropogenic sources such as combustion processes, or by eolian transport. CaSO_4 particles may be enriched in S and can therefore be partially identified as $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ resulting from coagulation of CaSO_4 with submicrometer sulphate aerosols. These findings are also in agreement with LAMMS analysis [9]. On the other hand, Ca-rich particles can also originate from the marine environment. Various dissolved salts begin to crystallize sequentially as seawater evaporates. Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) precipitate first, followed by CaSO_4 and the Mg-salts. It is possible that $\text{CaMg}(\text{CO}_3)_2$ undergoes further reaction with gaseous S-rich components. EPXMA measurements support the existence of such transformed particle species. Aluminosilicate particles cannot be distinguished from flyash particles on the base of their chemical composition. Only morphology can sometimes make the

differentiation. Important differences of these typical, nearly perfect, spherical flyash particles were observed in samples taken over the North Sea as air-mass backtrajectories originated from above Eastern Europe. A minor fraction of the quartz can be emitted during combustion processes of coal in power plants [14]. Titanium particles above the North Sea most probably find their origin on the continent and possible sources are paint spray, soil dispersion, asphalt production and power plants.

LAMMS studies have shown that the amount of nitrate coated seasalt particles increases significantly from a beach site in Brazil towards an industrialized area, 30 km downward from the ocean [15]. The detection of methanesulphonate, a biogenic airborne organic compound, above the Sargasso Sea, the Bahamas area [16], and the coast of Antarctica [4] constitutes an excellent illustration of the occasional "organic successes" of the LAMMS technique. By use of EPXMA it was found that high number concentrations of alumino-silicates present as internal mixture with sea salt aerosols over the Pacific Ocean are most likely the result of coagulation of sea salt and silicate particles within clouds, including droplet coalescence [17] rather than resuspension of silicate particles from the sea surface as a result of bubble bursting processes. More than 5,000 aerosol particles collected over the Eastern Equatorial Pacific from a sailboat (from Panama to Tahiti) were analyzed by EPXMA, combined with cluster techniques. The most abundant particle type was rich in S (45% of all particles) and this in the absence of other detectable elements. Morphological inspection of these particles allowed to differentiate between two groups, namely one group of S-rich particles in the sub-micrometer range that are unstable under the electron beam and are most probably $(\text{NH}_4)_2\text{SO}_4$, and one S-rich group in the micrometer range (mean particle diameter of 2 μm) showing more spherical contours. The latter group is much less affected by electron irradiation. The crustal component and also Cu and Zn are more abundant in those samples collected near the American continent. An important fraction of particles only yielded characteristic Ca and P X-rays; their mean diameter varied between 0.4 and 0.8 μm . Their abundance shows a slight tendency to increase as the sample location approaches the continent, but this is insufficient to conclude terrestrial sources to be responsible. It is known that the Pacific Ocean is slightly supersaturated in hydroxy-apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), but this, in turn, is not sufficient to suggest that the ocean is responsible for the production Ca-P-rich aerosols.

Urban aerosols

The composition of an urban aerosol will of course largely depend on its geographical location, the activities performed locally and the industries surrounding the sampling site. Automated EPXMA and LAMMS studies were performed on more than 15,000 individual Pb-containing particles sampled near the city of Antwerp, Belgium [18][19]. Soil dust particles are usually abundant. Other particle types often found are sulphates (CaSO_4 , fine and coarse sulphur-rich particles), auto exhausts (Pb-halides and sulphate derivatives) and different anthropogenic particles derived from various sources such as oil burning processes (S, V, Ni), abrasion processes (Fe-, Cr-oxides), and emissions of incinerators (Zn-, Pb-, Cu-, Zn- and Sb-rich particles). The principal source of particulate Pb in the urban atmosphere is the combustion of leaded petrol. Partial conversion of Pb-halide containing particles into Pb-sulphates often occurs by the reaction with ammonium sulphate present in the urban atmosphere. The ammonium sulphate can also be present as a coating on the Pb-containing particles.

Industrial and workplace aerosols

Industrial aerosol research is often concerned with the quality of the working environment. As toxic effects are often correlated with specific particles, shapes, sizes or element distributions, microanalysis is a very powerful tool to point out the dangerous parameters. Different asbestos types, which are known to promote fibrosis and/or cancer, can be distinguished on the base of their LAMMS spectra [20]. LAMMS and SIMS were also applied for the analysis of organic impurities at the surface of asbestos fibres [21][22]. The absorption behaviour of different asbestos varieties for various organics were studied by LAMMS [23][24]. Moreover, LAMMS revealed preferential leaching of elements in e.g. biological liquids. These results are of importance in the sense that, next to fibre geometry, chemical properties and reactivities also determine the carcinogenic effect.

Annegarn et al. [25] used automated EPXMA to analyze size-fractionated aerosol particles from a gold mine atmosphere. Silicon-rich particles were the most abundant, while chlorine-rich particles dominated the 0.2-1 μm size range.

Wouters [26] analyzed Cr-containing particles from pigmentation, soldering and plating industries by LAMMS. The anthropogenic Cr-particles appeared most of the time in the hexavalent (i.e. the most harmful) oxidation state. It should however be stressed that, in general, obtaining stoichiometric results with LAMMS is by no means straightforward.

Flyash is a much investigated type of industrial aerosol. This name covers a variety of particles. They are emitted to the atmosphere by combustors mostly used for the generation of electric power. Knowledge of the bulk composition of flyash is often insufficient because of the important internal composition heterogeneity within a particle population. Several workers have used SEM and/or EPXMA to determine the morphological and chemical

characteristics of flyash particles. The main elements present in both the micron and submicron particles are Si, Al, K, Fe, Ti, Mg and S, while Ca, P, Na, Cl and Ni are minor constituents. The major part of flyash particles have a characteristic spherical geometry although irregularly shaped particles are observed as well [14]. One should differentiate between two flyash types according to the fuel (oil or coal). Differences between oil flyash and coal flyash were reported by several authors [27][28]. Oil flyash particles vary in morphology from nearly rounded spheres to spongy lumps, which indicate a long exposure history to heat and oxidants. These spongy structures easily break down to smaller aggregates. Over 90 % of the mass fraction occurs in the fine fraction. Oil combustion particles contain considerably more sulphur and substantial amounts of V and Ni. Coal fly ash predominantly consists of smooth mineral spheres and contain less cenospheres. LAMMS of flyash particles in some occasions leads to the detection of PAH's [27]. PAH's were also detected using LAMMS on soot particles from an experimental oil-shale retort [29].

Sediments, suspension and estuarine/riverine particles

Suspended particulate matter from estuarine and marine environments is being investigated extensively in order to assess sedimentation processes, the interactions between sediments and the water column, and the physico-chemical reactions that particles undergo. Most of the analytical techniques used provide information on the bulk composition or mineralogy of the samples. Alternatively, beam techniques for individual analysis of estuarine particles can be invoked.

The first SEM/EDX studies in this field had in common that the particles were searched and analyzed manually for their chemical and morphological characteristics. The first results of automated EPXMA of marine suspended particulate matter were reported in 1982. Since then, various aquatic (estuarine and marine) environments have been studied, all by using automated EPXMA. Suspended matter particles from the Scheldt river estuary (Belgium, the Netherlands) have also been studied with LAMMS [6][30].

For all estuarine systems, EPXMA made it possible to evaluate the effect of mixing material from different origin and to separate the mixing process from other processes such as deposition and remobilization. The results on the Ems estuary (in Germany and the Netherlands) elucidated that the mixing with marine material occurs in the fresh water tidal area and that the suspended matter of marine origin is transported upstream the tidal, across the salt wedge [6]. The same approach proved to be equally successful when applied on the sediment fraction of the Elbe estuary (Germany), for which the findings were in agreement with those of the Ems river [31]. For the Garonne and Rhône river (France), no evidence was found for a net flux of marine suspended particulate matter into the estuaries; this is a consequence of the different nature of these estuaries [32][33].

For the Nile river (Egypt), no marine intrusion and thus no mixing process had to be taken into account; still significant relative abundance variations were observed for both the sediment and the suspended particulate matter. Information was gained on the impact of the Aswan Dam, the behaviour of the particles in this area and their further course along the Sohag area downstream [34].

For the Magela Creek river system (Australia) an advanced approach was achieved by analyzing both the suspension ($>1\ \mu\text{m}$) and colloidal ($1 - 0.1\ \mu\text{m}$) particles whereas most previous work was concentrated on the larger size suspended particulate matter (generally $>0.45\ \mu\text{m}$). The significance of these results lies in the fact that recent studies recognize an increasing importance of the role of this colloidal fraction for certain aquatic environments [35]. The inorganic mineral composition proved also to serve as an equally good tracer for the origin of suspended particulate matter of non fluvial estuarine environments.

The abundance variations of the particle types, correlated with hydrographical/hydrochemical and bulk data, provided information about geochemical and physical processes that influence the levels and distribution patterns of certain particle types throughout the Baltic Sea and the transient area to the North Sea [36].

A better insight in the sources and lateral/depth dispersal of suspended matter in Makasar Strait and Flores Sea and around the Sumbawa Island (Indonesia) was satisfactorily accomplished by EPXMA. It was found possible to differentiate between particles of terrestrial, volcanic and biogenic origin of the sediment [37].

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